Alkylate Measurements at Field Sites

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Sponsor, DOE Office of Fuels Development

Workshop on the Increased Use of Ethanol and Alkylates in Automotive Fuels in California

April 10-11, 2001

Oakland, CA

Presentation outline

- Alkylate compounds in current gasoline and their relationship to TPH-g and risk.

- Fate and transport issues in gasoline spills

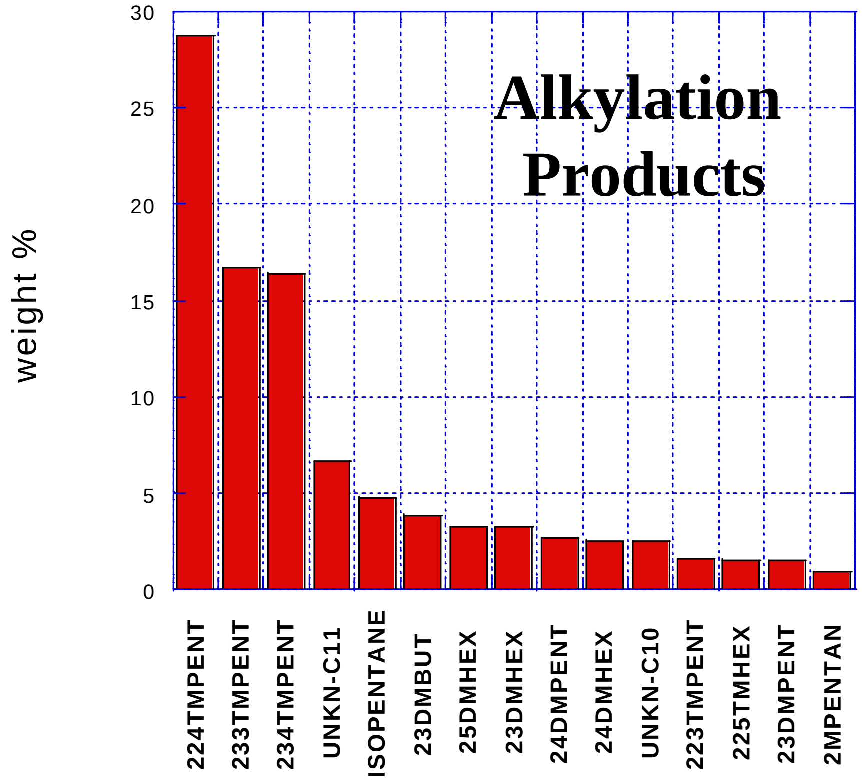
- Analytical measurements, field sites, and experimental approach.

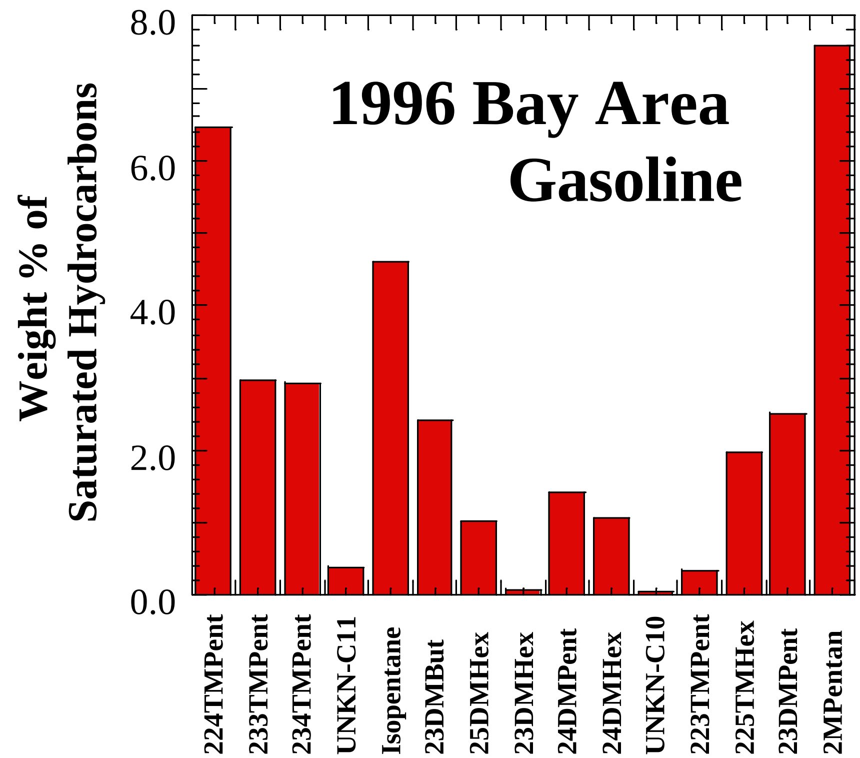
- Preliminary data

Estimated composition of California reformulated gasolines (from UCRL-AR-135949)

Fuel Component	MTBE-Blended	EtOH-Blended Volume %	No Oxygen
n-Butane	0.6	0.5	0.1
C_5 and C_6 alkanes	6.1	4.3	11.3
C_7 to C_9 branched alkanes	14.4	28.4	32.5
Benzene	0.67	0.80	0.80
Total aromatics	24.0	20.0	20
Total olefins	4.3	2.9	5.0
Oxygenate	11.4	7.8	0
Other	39	35	30
Total	100.47	99.7	100
Oxygen (wt%)	2.1	2.7	--

Alkylates already occur in gasoline





Data from STRATCO

Production Profile

Percentages are in agreement with those presented by Durett *et al.* for a finished alkylate (*Anal. Chem.* **35** pp 637, 1963)

Weight percent of total n-alkanes, isoalkanes, and cycloalkanes in 1996 Bay Area gasoline (Kirchstetter et al., 1999).

Physicochemical properties for MTBE, ethanol, and isooctane

Property	Units	Fuel Compound: MTBE	Ethanol	Isooctane
Molecular weight	g/mol	88.15	46.7	114.23
Weight % Oxygen		18.2	34.8	0
Octane rating		110	115	100
Density as liquid	g/mL	0.740	0.789	0.69
K_{ow}	dimensionless	8.71	0.50	12,200
Vapor pressure†	Pa	32,664	7,869	6,490
Solubility	mg/L	48,000	Miscible	2.4
Henry's law†	Pa-m^3/mol	53.5	0.64	323,000

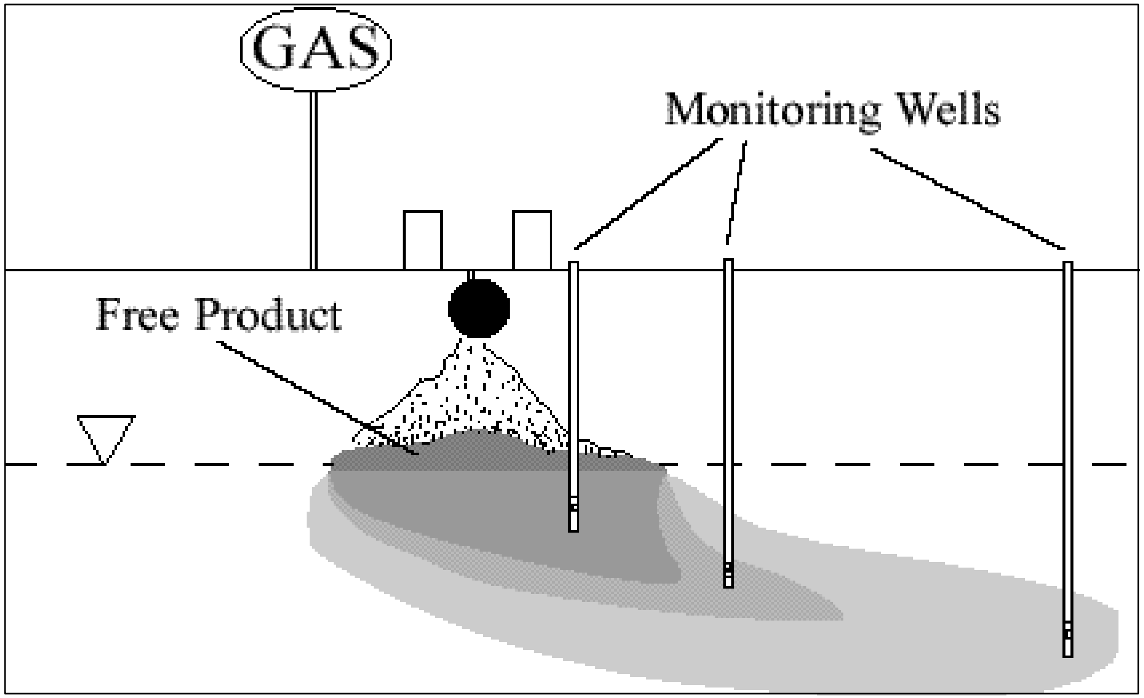
Where's the data?

- Previous field studies on gasoline spills focused on fate and transport of BTEX and oxygenates.
- Regulatory mandate mostly requires quantification of carcinogens and TPH-g.
- TPH-g is not compound specific and often semi-quantitative.
- Biodegradation studies are limited for branched alkanes.

TPHCWG recommendations

- Carcinogenic risk based on indicator compounds of benzene and PAHs.
- Non-carcinogenic risk based on fraction-specific toxicity criteria. Fractions determined by carbon number. e.g. RfDs: Benzene < C6-C9 < C10-C12
- Risk assessment based on exposure pathways and toxicity criteria.
- Update approach as data become available on fate, transport, and toxicity of TPH constituents.

Measurement approach



Data Collection
- Field Parameters
- BTEX and MTBE
- TPH-g
- Hydrocarbons
- Total non-volatile
- Carbon isotopes

Uncertainties
- Exact age and character of spill is typically not known.
- Sample reproducibility may be an issue for alkylates.
- Site-to-site variability may be large due to differences in environment, well construction, sampling method, etc.

Hydrocarbon measurements

Target compounds are alkanes greater than 1% by weight in commercial gasoline:

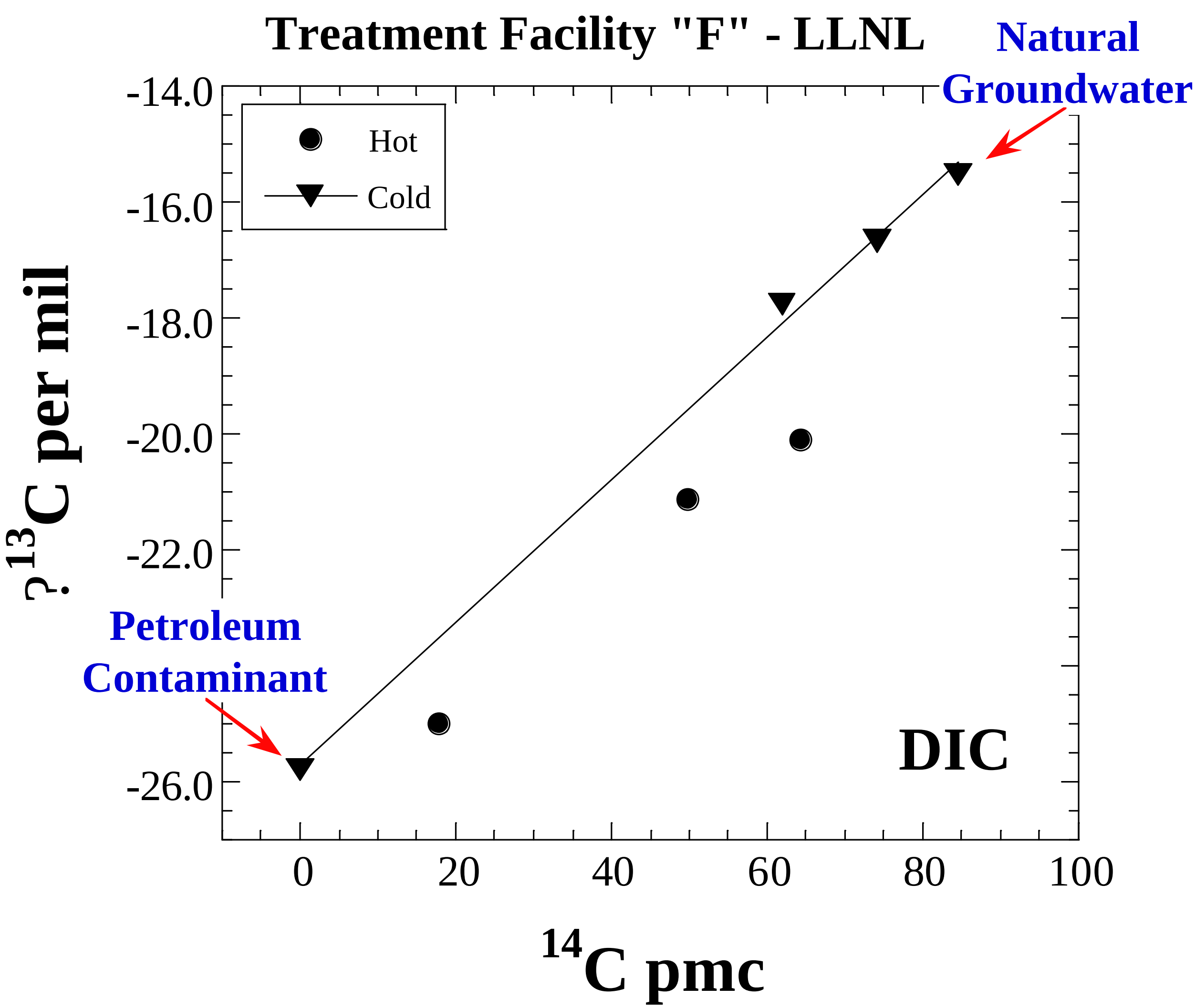
n-alkanes
n-pentane
n-hexane
n-heptane
n-octane

isoalkanes
2-methylbutane
2-methylpentane
3-methylpentane
2,2,4-trimethylpentane
2,3,3-trimethylpentane
2,3,4-trimethylpentane
2,2,5-trimethylhexane

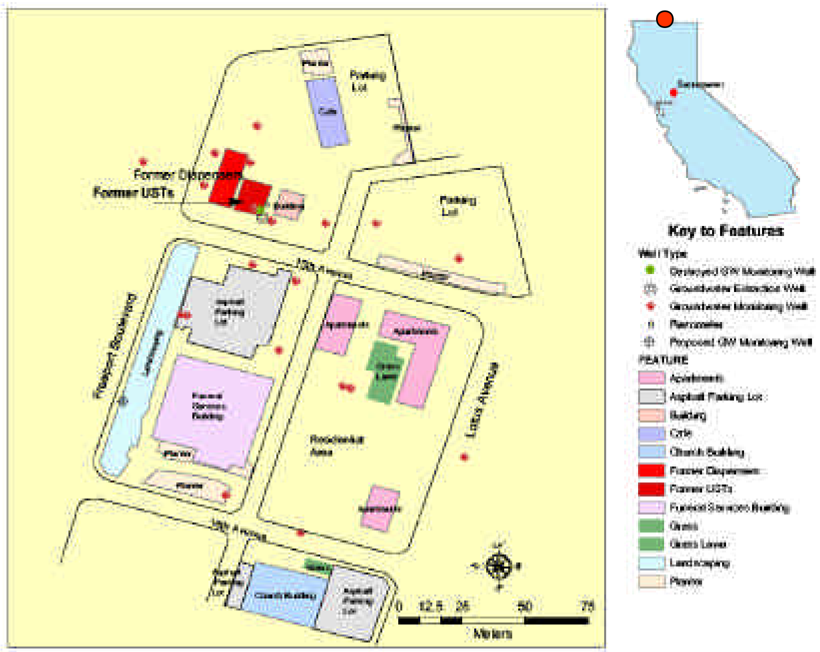
cycloalkanes
methylcyclopentane
cyclohexane
methylcyclohexane

Initial measurements were preformed by GC/FID using modified EPA 8015 and 8021 methods. Developing GC/MS method.

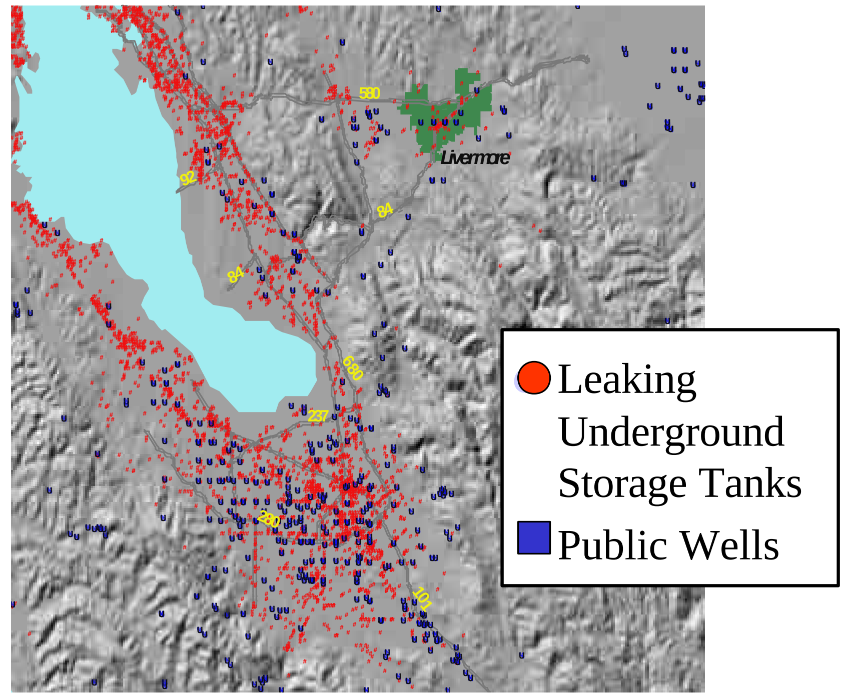
Isotope mass balance of biodegradation



Two UST sampling sites were selected



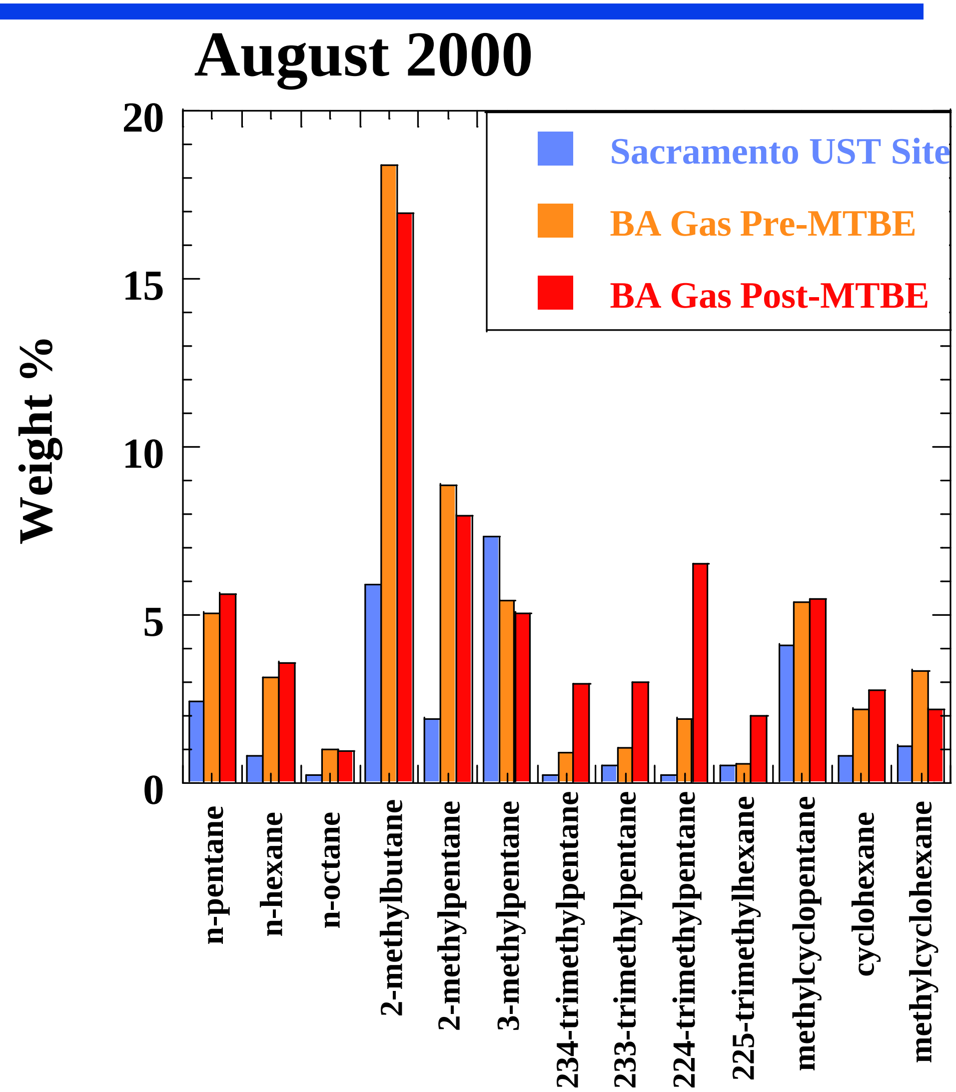
Sacramento
ETIC cooperation



San Jose
SCVWD cooperation

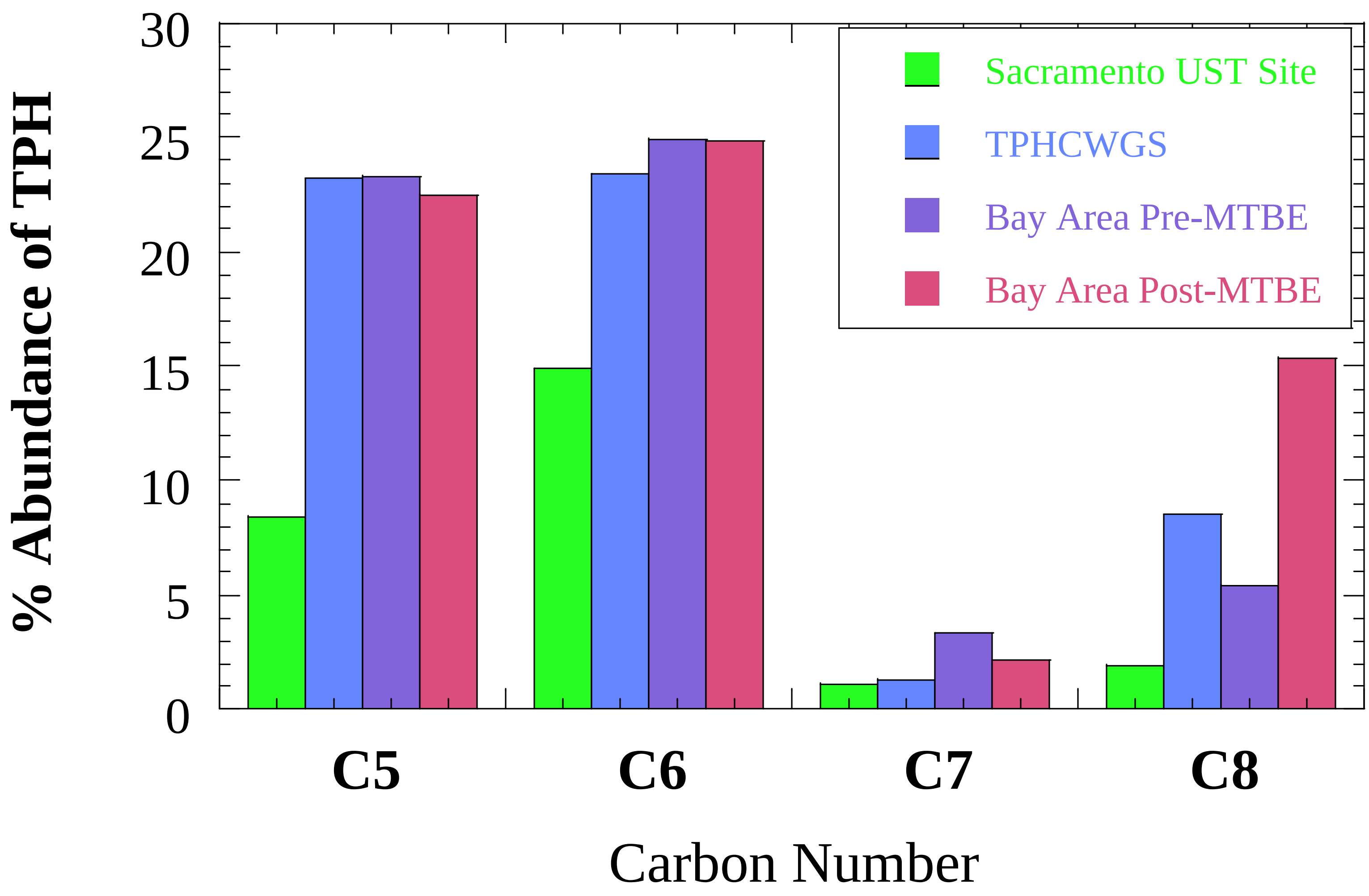
BTEX is 10X Greater than Branched Alkanes

	Avg. mg/L Sacramento
n-pentane	0.86
n-hexane	0.30
n-octane	0.10
2-methylbutane	2.18
2-methylpentane	0.73
3-methylpentane	2.73
234-trimethylpentane	0.12
233-trimethylpentane	0.22
224-trimethylpentane	0.10
225-trimethylhexane	0.23
methylcyclopentane	1.49
cyclohexane	0.33
methylcyclohexane	0.43
Benzene	27.0
Toluene	18.0
Ethyl-Benzene	3.9
Xylenes	23.0



Reportable detection limit is 0.1mg/L

TPH-g constituents roughly scale to parent gasoline



Summary statements

- Minor increases in alkylates probably will occur in subsurface spill sites.
- Persistence of isooctane and other branched alkanes in groundwater is poorly understood relative to BTEX.
- Even less understood for a gasohol spill
- Toxicological risk of these alkanes is 10X less than benzene.
- Any persistence of alkylates in groundwater would probably be more of a taste and odor issue.